ON THE FATTY ACIDS OF JAPAN WAX.

By **Mitsumaru TSUJIMOTO.**

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The chemical composition of Japan wax (fruit-coat fat from the berries of "Hazé", *Rhus succedanea* L.) was chiefly investigated by foreign chemists and the specimens used by them were the bleached white wax. As the results of these researches Japan wax has been ascertained to consist mainly of tripalmitin and free palmitic acid. Besides them, of saturated acids small amounts of dibasic acids and of soluble acids (isobutyric?) were found. In some old books on fats and oils, stearic and arachidic acids were mentioned to occur in Japan wax. However, they could not be detected by A. C. Geitel and G. van der Want.(1) In the modern books, these acids, especially the latter, are usually omitted. Of unsaturated acids a small amount of oleic acid was stated to occur. Later Tassily(2) isolated pelargonic acid and an acid of the suggested formula $C_{15}H_{30}O_2$. Traces of stearic and oleic acids were also detected.

It is no wonder that oleic acid in Japan wax was rather neglected by foreign investigators, inasmuch as it is markedly changed or oxidised by the severe treatment of insolation on bleaching the wax. Also the presence of volatile or soluble acids is due to sun-bleaching process.

More than twenty years ago, the author(3) suggested the following composition of Japan wax fatty acids: palmitic acid 84%, oleic acid 14%, japanic acid(?) 2%. Nowadays the above amount of the dibasic acids has been found to be too small.(4)

The present experiments were made to reconfirm the components of the fatty acids (the dibasic acids being excepted) of genuine Japan wax. As the results the occurrence of stearic and arachidic acids has been ascertained, thus confirming the correctness of the description of the old books.

Experimental Part.

(1) **General Properties of the Specimen of Japan Wax.** The specimen used in this investigation was a raw or fresh wax, especially prepared from the berries

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(1) *J. prakt. Chem.*, **61** (1900), 151.
(2) J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Vol. II (5th Edition), 654.
(3) *J. Soc. Chem. Ind. Japan*, **14** (1911), 321.
(4) Concerning the dibasic acids see M. Tsujimoto, this Bulletin, **6** (1931), 325.

("Komi"⁽⁵⁾ or old berries) of *Rhus succedaneae* L. from the Prefecture of Kumamoto by the Higo Seirô Kaisha (Higo Wax Manufacturing Company), which contained no kernel oil.⁽⁶⁾

It was a brownish-yellow solid, which, though coherent and tenacious, was rather brittle. The characteristics, etc., were as follows:⁽⁷⁾ Melt. pt. 53–53.5°C., d_4^{99} 0.8608, acid value 15.9, saponification value 208.1, iodine value 13.4, Reichert-Meissl value 0.38, unsaponifiable matter 0.77%.

As the specimen was free from the kernel oil, its iodine value was lower than those of commercial samples (iodine value, sometimes up to 20). The Reichert-Meissl value was very small indicating a negligible amount of volatile water-soluble acids.

The unsaponifiable matter was a brownish-yellow fine crystalline mass and produced a large amount of precipitate with digitonin in alcoholic solution.

The fatty acids formed a brownish-yellow crystalline mass of the following properties: Melt. pt. 63°C. (mainly liquefied at 61–62°C.), neutralisation value 215.3, iodine value 12.7, dibasic acids 6.3%.

The fatty acids were dissolved in acetone and on cooling the deposited solid acids were separated. By concentrating the filtrate, the crystallisation was repeated several times. The liquid acids were separated from the acids of the final filtrate by means of the lead-salt-ether method. They were of a brownish-yellow colour and had neutralisation value 193.1, iodine value 87.1, and n_D^{20} 1.4620. These figures nearly corresponded to those of oleic acid. On bromination in petroleum ether solution, they gave a small amount (ca. 1.7%) of a white precipitate; in ether solution, a little turbidity was observed, but nearly no precipitate. It appeared, therefore, that there occurred in the liquid acids a small proportion of linolic acid, but linolenic acid was almost absent in them.

(2) **Identification of the Component Fatty Acids.** The mixed fatty acids (unsaponifiable matter not removed) from the specimen of Japan wax were changed into methyl esters by boiling with half the weight of methanol containing 3% of H_2SO_4 upon a water bath for three hours. The ester mixture thus obtained was a brownish-yellow liquid in summer; it had still acid value 2.34, but was used without further treatment.

The methyl esters (1000 g.) were distilled (in batches of 250 g.) under 15 mm. pressure into the following fractions:

Fract.	Dist. temp.	Yield		Saponif. value	Iodine value	n_D^{20}
		(g.)	(%)			
I	Up to 200°	555.3	55.5	2.5.9	7.4	1.4389
II	200–205°	221.1	22.1	202.8	13.0	1.4395
III	205–210°	77.6	7.8	201.6	20.5	1.4410
IV	210–219°	60.2	6.0	198.7	32.1	1.4430

Distillates (total) 914.3 g. (91.4%). Residue 85.2 g. (8.5%)

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(5) This Bulletin, **6** (1931), 326, foot-note.

(6) According to the author's experiments, the kernels of the berries of *Rhus succedanea* contained 4–9% of the oil. The oil had the following properties: d_4^{15} 0.9254–0.9289, acid value 2.16–4.32, saponification value 189.6–193.6, iodine value 125.2–133.2.

(7) All the iodine values were determined by Wijs method.

The residue consisted mainly of the methyl esters of the dibasic acids and the unsaponifiable matter.

The fractions were re-distilled under 15 mm. pressure. The results corresponding to 950 g. of the original esters were as follows:(8)

Fract.	Dist. temp.	Yield		Appearance (at 20°C.)	Saponif. value	Iodine value	n_D^{20}
		(g.)	(%)				
1	Up to 190°	0.7	0.07	White crystals	204.3	—	1.4375
2	190–200°	632.7	66.6	,,	205.0	6.2	1.4380
3	200–205°	120.6	12.7	White crystals and a little liquid	200.6	19.0	1.4400
4	205–210°	56.0	5.9	Nearly colourless liquid	198.6	26.7	1.4415
5	210–215°	23.8	2.5	,,	195.7	36.9	1.4431
6	215–222°	22.4	2.4	Pale yellow liquid	193.6	42.9	1.4450

Distillates (total) 856.2 g. (90.1%). Residue (brownish-yellow, crystalline mass) 11.0 g. (1.2%).

The distillation temperature soon rose above 180°C. The residue of the first fractionation was not re-distilled.

The fractions, especially the higher-boiling ones, showed notable unsaturation; this was apparently due to the methyl ester of oleic acid.

Each fraction was then examined for its component fatty acids.

Fraction 1 (up to 190°C./15 mm.). The yield was very small. Judged from its boiling point and saponification value, myristic acid and the lower homologues appeared not to be present. The free acid obtained from it, when crystallised from 90% alcohol, melted at 63°C., and by mixed test, was identified to be palmitic acid.

Fraction 2 (190–200°C./15 mm.). This was the principal constituent of the esters. To separate the solid part, 600 g. of the fraction was dissolved in about twice of its volume of acetone and well cooled with ice; the deposited solid was separated by a suction funnel. From the filtrate the acetone was distilled, and the remaining substance was again treated similarly. By these treatments 388 g. of a solid substance was obtained. It formed a beautiful, white crystals of m.p. 29°C., saponification value 206.7 and iodine value 0.64. Although it contained a very small amount of unsaturated substance, its properties nearly coincided with those of methyl palmitate (m.p. 30°C., saponif. value 207.6). The free acid obtained from it by saponification, on crystallising from alcohol, melted at 62°C. and had neutralisation value 218.7. So it consisted of palmitic acid (m.p. 62.6°C., neutr. value 218.9).

From the acetone-filtrate the solvent was distilled off, and on saponifying the remaining esters, 196. g. of fatty acids comparatively rich in liquid components were obtained. These were dissolved in four times of their volume of acetone, and kept at 18–20°C. overnight; the deposited solid was separated and the filtrate was again treated similarly.

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(8) Though not strictly accurate, the following procedure was adopted. A fraction was distilled to a prescribed temperature and the residue was mixed to the next fraction and distilled; the distillate coming over to the temperature was mixed to the former fraction.

Such treatment was repeated several times, finally by cooling with ice. As the result, 170 g. of solid acids and 25 g. of crude liquid acids were obtained.

The solid acids melted at 60–60.5°C. and had neutralisation value 212.3 and iodine value 7.8. By crystallising the acids from alcohol, palmitic acid was isolated.

The crude liquid acids had iodine value 73.7 and were still admixed with solids. They were dissolved in 250 c.c. of 95% alcohol, and while hot, 5 g. of lead acetate was added to complete solution. On keeping at room temperature (18°C.) for five hours, the precipitate was filtered off, and on decomposing the insoluble and soluble lead salts, 5.8 g. of solid acids and 18.5 g. of liquid acids were obtained.

The solid acids had neutralisation value 203.4 and iodine value 53.9; so they contained more than half of the weight of unsaturated acids. On crystallisation from alcohol, the crystals melted at 52–52.5°C. By mixed test the chief component appeared to be palmitic acid.

The liquid acids were of an orange-yellow colour and had neutralisation value 194.7, iodine value 86.5, and n_D^{20} 1.4590. They were changed into methyl esters, and 18 g. of the esters were fractionally distilled under ca. 15 mm. pressure. The results were as follows:

Fract.	Dist. temp.	Yield (g.)	Appearance	Saponif. value	Iodine value	n_D^{20}
a	Up to 200°	0.5	Pale yellow liquid	179.9	70.5	1.4500
b	200–210°	10.8	,, ,, ,,	189.5	79.6	1.4520
c	210–216°	5.5	Light yellow liquid	187.8	83.9	1.4520

Residue (brownish-yellow liquid) 0.5 g.

The amount of fraction a was very small; its low saponification value was caused by the admixture of the remaining solvent. The fatty acids from this fraction had neutralisation value 193.5.

The saponification and iodine values of fractions b and c nearly corresponded to those of methyl oleate (saponif. value 189.3, iodine value 85.7). By the elaidin test (Hg and HNO_3), the free acids from these fractions solidified easily and gave elaidic acid of m.p. 44–44.5°C. The acids consisted, therefore, mainly of oleic acid. Hexadecenoic acid, $C_{16}H_{30}O_2$, did not appeared to occur in the present specimen of Japan wax. The presence of the oleic ester in the comparatively low-boiling fraction was due to the fact that a small amount of it was carried over with a large amount of methyl palmitate in the distillation.

Fraction 3 (200–205°C./15 mm.). On saponification, 111.7 g. of the fatty acids were obtained from 117 g. of this fraction. They were treated with acetone and then separated into solid and liquid acids by the lead-salt-alcohol method in the similar manner as described in the case of the previous fraction. Thus the acids were separated as follows:

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (A) deposited from acetone	97	209.3	12.0
,, ,, (B) obtained by lead-salt-alcohol method	4.6	206.5	32.3
Liquid acids ,, ,, ,,	10	197.7	84.8

On crystallising solid acids A from 90% alcohol, crystals of m.p. 60–60.5°C. were obtained; by mixed test they were identified to be palmitic acid. Solid acids B melted, after second recrystallisation, at 53–53.5°C.; the main component of their saturated acids consisted also of palmitic acid. By the elaidin test, the liquid acids were confirmed to consist mainly of oleic acid.

Fraction 4 (205–210°C./15 mm.). The fraction (54 g.) gave 51.4 g. of the fatty acids, which were treated similarly as previously described.

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (C) deposited from acetone	38	207.1	14.6
,, ,, (D) obtained by lead-salt-alcohol method	4.7	208.3	37.1
Liquid acids ,, ,, ,,	8.1	196.6	87.6

Solid acids C, when recrystallised from 90% alcohol, melted at 55°C.; the high boiling point of the fraction indicated the presence of some saturated acids (possibly stearic acid) higher than palmitic acid. Solid acids D melted, after recrystallisation, at 53°C.; they appeared still to contain palmitic acid. The liquid acids consisted mostly of oleic acid.

Fraction 5 (210–215°C./15 mm.). This fraction was mostly liquid at 15°C., though a notable amount of crystals was deposited. On saponification 20.9 g. of the fatty acids were obtained from 22 g. of the fraction. They were dissolved in 70% acetone and cooled with ice; the deposited solid acids were separated from the solution. The fatty acids remaining on evaporating off the acetone were then dissolved in 100 c.c. of 95% alcohol, and the still admixed solid acids were precipitated by adding 1 g. of lead acetate. By these procedures the following results were obtained:

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (E) deposited from acetone	12.6	51–52°	206.0	12.0	—
Solid acids (F) obtained by lead-salt-alcohol method	1.2	61°	213.1	23.5	—
Liquid acids ,, ,, ,, ,,	7.1	—	198.7	85.6	1.4600

Solid acids E (10 g.) were dissolved in 300 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate as follows:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.9	57 – 57.5°C.	201.2
,, ,, ,, 2nd ,,	1.9	54.5–55°C.	205.2
,, ,, ,, 3rd ,,	1.8	54 – 54.5°C.	208.4
,, ,, ,, 4th ,,	1.9	54 – 54.5°C.	212.7
,, ,, ,, 5th ,,	1.5	57 – 57.5°C.	212.8

As the above results show, besides palmitic acid, the presence of stearic acid in the acids would be expected. By fractionally precipitating the fatty acids from the 1st precipitate, 0.3 g. of a solid of m.p. 61.5–62°C. and neutralisation value 189.9 was obtained. Judged from the neutralisation value, this substance appeared to be a mixture of stearic and the higher saturated acids.

Solid acids F contained a fairly large amount of unsaturated acids; as the neutralisation value was high, their main component was probably palmitic acid.

The liquid acids readily formed elaidic acid (m.p. 43.5–44°C.), so the main component was oleic acid.

Fraction 6 (215–222°C./15 mm.). This fraction formed a soft crystalline mass at 15°C. It (20 g.) gave 19.3 g. of the fatty acids, which were treated in the same way as those of preceding fraction.

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (G) deposited from acetone	8.1	64°C. (mainly liquid at 60°C.)	202.5	0.8	—
Solid acids (H) obtained by lead-salt-alcohol method	2.6	52°C.	213.2	37.4	—
Liquid acids ,, ,, ,, ,,	8.3	—	195.2	86.2	1.4600

The solid acids G consisted mostly of saturated acids. As they were found to contain a small amount of the dibasic acids, 7.8 g. of them were dissolved in about 50 times of their volume of petroleum ether in the hot and kept at room temperature of 22–25°C; the deposited dibasic acids (0.4 g.) were then filtered off.

The acids (6.5 g.) thus freed from the dibasic acids were dissolved in 200 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate.

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.5	61 – 61.5°C.	192.3
,, ,, ,, 2nd ,,	1.5	60 – 60.5°C.	195.8
,, ,, ,, 3rd ,,	1.8	60.5–61°C.	202.1
,, ,, ,, 4th ,,	1.3	55 – 55.5°C.	208.8

The last mother liquor gave, on evaporation, a soft crystalline mass.

The fatty acids from the 1st and 2nd precipitates were mixed and repeatedly recrystallised from alcohol with the following results:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st recrystallisation	1.4	63°C.	—
,, ,, ,, 2nd ,,	0.8	64.5–65°C.	—
,, ,, ,, 3rd ,,	0.4	70 – 70.5°C.	183.5

The last acids, when mixed with an equal part of arachidic acid (m.p. of the specimen 75°C.), melted at 72–72.5°C. On analysis the substance gave the following results: Found: C, 76.80; H, 13.06. Calc. for $C_{20}H_{40}O_2$: C, 76.84; H, 12.91%. The substance was, therefore, confirmed to be somewhat impure arachidic acid (m.p. 77°C., neutr. value 179.6).

The mother liquor of the arachidic acid was twice concentrated, the deposited solid (yield ca. 1 g.) separated, and on further concentration 0.45 g. of crystals was obtained.

This substance melted at 63–64°C. and had neutralisation value 194.0; mixed with stearic acid (equal part) it melted at 66–66.5°C. Found: C, 75.44; H, 12.93. Calc. for $C_{18}H_{36}O_2$: C, 75.98; H, 12.76%. Thus the substance consisted of stearic acid.

The acids intermediately deposited (neutr. value 188.3 and 193.5) were mixtures of arachidic and stearic acids.

The fatty acids from the 4th precipitate appeared to be a mixture of stearic and palmitic acids.

The solid acids H contained a notable amount of unsaturated acids; on crystallising them from 90% alcohol, crystals having m.p. 57–58°C. and neutralisation value 212.2 were obtained, so they consisted mainly of palmitic acid. It was rather unexpected to find the presence of palmitic acid in such a high-boiling fraction, though the amount was very small; this indicated the difficulty of thoroughly separating fatty acids from one another by simple fractional distillation of their methyl esters.

The liquid acids formed elaidic acid of m.p. 43.5°C., so they were identified to be oleic acid.

The distillation residue of the second fractionation of the original esters consisted mainly of the esters of the dibasic acids. It should be noted that notwithstanding their high boiling points these esters distilled over together with those of the fatty acids, but their amount was comparatively small.

(3) **On the Free Fatty Acids in Japan Wax** The amounts of free acids in commercial samples of Japan wax vary somewhat markedly and are usually rather high, but the unbleached wax contains a far smaller amount than the sun-bleached one. The following brief experiment was performed to ascertain the components of the free acids.

The specimen of Japan wax (50 g.) was heated with 200 c.c. of 90% alcohol to dissolve out the free acids; on cooling the wax sank and solidified, hereupon the upper solution was decanted. The wax was again treated with 100 c.c. of alcohol. The alcoholic solutions, which deposited notable amounts of solids, were united, neutralised with alcoholic NaOH solution, and evaporated to dryness. The solid residue was mixed with sand and extracted with petroleum ether in a Soxhlet apparatus to remove neutral wax. The soap was then decomposed with diluted hydrochloric acid.

The free acids thus separated amounted to 2.7 g. They formed a pale brownish-yellow solid, and had neutralisation value 195.4, saponification value 212.9, and iodine value 26.7; the content of the dibasic acids was 5.1%. A further treatment of the extraction of neutral wax was made to ensure the complete removal of it. Then the acids had neutralisation value 206.2 and iodine value 27.1.

From the above results, it has been concluded that the components of the free acids were nearly the same as the mixed acids of the wax, but oleic acid was present in a far larger proportion.

Summary.

The component fatty acids of a specimen of unbleached Japan wax, which contains no kernel oil, have been examined.

In agreement with the description in fat literature, palmitic acid is, of course, the main component. Myristic acid and the lower homologues appear not to be present; volatile lower acids stated to occur in Japan wax by old investigators are undoubtedly decomposition products formed by bleaching process. On the other hand, stearic and arachidic acids occur in appreciable proportions. The unsaturated acids consist mostly of oleic acid. A small proportion of linolic acid is present. Hexadecenoic and linolenic acids are probably not present.

It is difficult to mention the quantitative proportion of the individual acids, but rough approximation would be as follows: Palmitic acid 77%, stearic and arachidic acids 5%, oleic acid 12%, linolic acid small amount (less than 1%), dibasic acids 6%.

The above proportion of stearic and arachidic acids would be rather high; in their relative amounts the former seems to predominate.

It is interesting to observe that whereas myristic acid can not be detected in Japan wax obtained from *Rhus succedanea,* it occurs abundantly in the wax of "Tsutaurushi", *Rhus toxicodendron, var. vulgaris,* a viny shrub belonging to the same genus *Rhus.*(9)

The free acids in Japan wax have nearly the same composition as the mixed acids of the wax, but oleic acid is present in a far larger proportion.

Tokyo Imperial Industrial Research Laboratory,
Hatagayacho, Shibuya, Tokyo.

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(9) This Bulletin, **6** (1931), 340, foot-note.